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(71) Applicant: Sulzer Metco Japan Ltd.  
Tokyo 102 (JP)

(72) Inventors:  
• Masahiro, Nakagawa  
Chiyoda-ku, Tokyo 102 (JP)

- Sasaki, Matisumasa  
Chiyoda-ku, Tokyo 102 (JP)
- Mima, Hidetada  
Chiyoda-ku, Tokyo 102 (JP)
- Hashimoto, Hiroyuki  
Chiyoda-ku, Tokyo 102 (JP)
- Hotta, Toshio  
Chiyoda-ku, Tokyo 102 (JP)
- Miyazaki, Tomoko  
Chiyoda-ku, Tokyo 102 (JP)

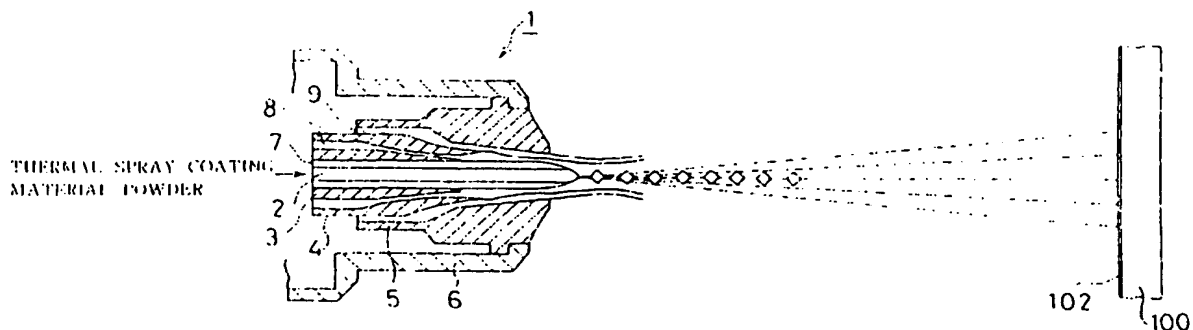
(74) Representative: Harvey, David Gareth et al  
Graham Watt & Co.  
Riverhead  
Sevenoaks Kent TN13 2BN (GB)

(54) High speed thermal spray coating method

(57) In a thermal spray coating method, a high speed flame is produced by using a combustion gas and then thermal spray coating material powder is sprayed by flame gun (1) onto a receiving surface (100) of a base material by using the high speed flame to form a coating

(102) on the base material. As the thermal spray coating material powder, a mixed powder is used, which contains (A) 98-70% by volume of Cu based lead bronze alloy powder and (B) 2-30% by volume of Al powder or Al based alloy powder.

FIG. 1



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## Description

This invention relates to a high speed thermal spray coating method in which a high speed flame is produced by using a combustion gas and thermal spray coating material powder is sprayed by using this high speed flame onto the surface of a base material to be thermal spray coated, thus forming a coating on the surface of the base material. In particular this method is suitable for forming a coating with improved lubricity and abrasion resistance on a part of the surface or the entire surface of a swash plate for an air compressor pump manufactured of aluminum alloy, cast iron or steel based alloy

Heretofore, the swash plate of an air compressor pump, for example, is structured in such a manner that the swash plate rotates to reciprocally move a piston through shoes which are in contact with the circumferential part of both surfaces of the swash plate, and therefore the shoes slidingly move over the peripheral surfaces of the swash plate.

The swash plate is ordinarily made of aluminum alloy, cast iron or steel based alloy, whereas the sliding shoes of mating parts are formed of SUJ2 (Japanese Industrial Standards), and when lubrication becomes insufficient, seizure is apt to occur. Therefore, an Sn plating or Teflon® (tetrafluoroethylene resin) coating is, heretofore, provided on the surfaces of the swash plate, and in addition, a treatment such as a coating of MoS<sub>2</sub> (lubricant) is applied thereon.

However, in the even the Sn-plated swash plate reaches a non-lubricated state and yet is placed under an operating condition in which the swash plate rotates with a high speed and bears a high load, abrasion loss on the surface of the swash plate increases, eventually ending in seizure taking place between the swash plate and the shoe. The Sn plating process takes about 30 minutes to form a plated layer of 10 µm thick, and further it needs portions of the swash plate not requiring the plating to be masked, which takes a lot of time for the coating and removing of masking material and as such has inferior workability.

Similarly, when a Teflon-coated swash plate is in a non-lubricated state and is placed under an operating condition requiring high speed rotation and high load bearing, the abrasion loss on the swash plate surface increases. It is also necessary when performing the Teflon coating to mask the portions of the swash plate surface not requiring the coating, which takes a substantial length of time, thus making the coating process rather troublesome.

At present, as far as the inventors know, there is no coating material suitable for a swash plate made of, for example aluminum alloy, cast iron or steel based alloy, which relative to shoes made of SUJ2, exhibits satisfactory abrasion resistance, scuff resistance or seizure resistance and pressure resistance under the conditions of a high speed rotation, high load and absence of lubrication.

Further, there is no method for improving surface properties which is capable of easily masking portions not required to have a coating using a wet process, as well as quickly removing the mask after forming the coating and also forming the coating at high speed.

Therefore, one of the objects of the invention is to provide a high speed thermal spray coating method in which the surface of the base material can be thermal spray coated with a coating which has satisfactory abrasion resistance, scuff resistance and pressure resistance under the conditions of high speed rotation, high load and non-lubrication, with a high speed and in an easy manner.

Another object of the invention is to provide a high speed thermal spray coating method capable of forming a coating which does not peel off when machining the coating, permits sound machine finishing without voids or porosity and further, has superior adhesion property.

Still another object of the invention is to provide a high speed thermal spray coating method capable of forming a coating which has satisfactory lubricity and abrasion resistance, on portions of the surface or the entire surface of a swash plate, for an air compressor pump, made of aluminum alloy, cast iron or steel based alloy.

The objects mentioned above can be achieved by the high speed thermal spray coating method according to the present invention. In brief, the invention is a high speed thermal spray coating method in which a high speed flame is produced by using a combustion gas and thermal spray coating material powder is sprayed by using said high speed flame onto the surface of a base material to be thermal spray coated to form a coating on the surface of the base material, characterized in that for said thermal coating material powder a mixed powder is used, said mixed powder containing:

- (A) 98-70% in volume of Cu based lead bronze alloy powder, and
- (B) 2-30% in volume of Al powder or Al based alloy powder.

By way of example, the Cu based lead bronze alloy powder comprises Cu based lead bronze alloy containing as its components Cu = 77-89% by weight, Sn = 4-11% by weight and the balance being impurities of 1% or less by weight. The Al powder preferably comprises Al containing less than 1.5% by weight of impurities, while said Al based alloy powder preferably comprises Al based alloy containing as its components Al = 65-95% by weight, Si = 4-30% by weight, Cu = 0.5-6% by weight, and Mg = 0.3-12% by weight. More preferably, the Cu based lead bronze alloy comprises Cu = 77-86% by weight, Sn = 6-9% by weight, and the balance being impurities of less than 1.0% by weight, while said Al based alloy powder comprises Al = 65-91% by weight, Si = 8-25% by weight, Cu = 2-4% by weight, Mg = 0.5-6%

by weight, and the balance being impurities of less than 0.5% by weight

Desirably each of said Cu based lead bronze alloy powder, said Al powder and said Al based alloy powder has a particle diameter of 10-75  $\mu\text{m}$ , and preferably 10-60  $\mu\text{m}$ , in particular 10-45  $\mu\text{m}$  for said Al powder and said Al based alloy powder

According to a preferable embodiment of this invention, said base material is subjected to a grit blast treatment on the surface of the said base material so as to have a surface roughness of  $\mu\text{Rz} = 10-60$ , is heated to 50-150  $^{\circ}\text{C}$ , and is then thermal spray coated to form a coating having a thickness of 0.2-0.5 mm on the surface of said base material. Further, said thermal spray coating can be performed by using as said combustion gas any one of mixed gases comprising oxygen/propane, oxygen/propylene, oxygen/natural gas, oxygen/ethylene, oxygen/ethylene, oxygen/kerosene and oxygen/hydrogen to generate a high speed flame having a flame speed of 1000-2500 m/second and a flame temperature of 2200-3000  $^{\circ}\text{C}$ , while maintaining a thermal spray coating distance at 170-350 mm and controlling a coating temperature during thermal spray coating to 200 $^{\circ}\text{C}$  or below.

Also according to the most preferable embodiment of this invention, said coating formed on the surface of the base material is finished to have a surface roughness of  $\text{Ra} = 0.4-6.0\text{ S}$ .

The thermal spray coating method of the invention is suitable for spray coating swash plates, manufactured of aluminum alloy, cast iron or a steel family alloy, for an air compressor pump.

The preferred practice of the present invention will now be described by way of example with reference to the accompanying drawings, in which:

Fig. 1 is a drawing showing a schematic structure of a thermal spray coating gun for carrying out the high speed thermal spray coating method of the invention,

Fig. 2 is a drawing showing pressure resistance of the thermal spray coatings obtained by the high speed thermal spray coating method according to the invention and that of the thermal spray coatings obtained by comparative examples;

Fig. 3 is a drawing showing abrasion resistance of the thermal spray coatings obtained by the high speed thermal spray coating method according to the invention and that of the thermal spray coatings obtained by comparative examples; and

Fig. 4 is a drawing showing seizure load of the thermal spray coatings obtained by the high speed thermal spray coating method according to the invention and that of the thermal spray coatings obtained by comparative examples.

Now, a high speed thermal spray coating method according to the present invention will be explained in further detail by referring to the drawings.

A schematic configuration of a thermal spray coating device (thermal spray coating gun) 1 for performing the high speed thermal spray coating method of the invention is shown in Figure 1. In brief, the thermal spray coating gun 1 has a powder projection port 2 positioned at the center part of the gun for projecting thermal spray coating material powder, and a nozzle insert 3, a shell 4 and an air cap 5 positioned concentrically from interior to exterior thereof, thus forming a combustion gas passage 8 and compressed air passages 7 and 9. Further, an air cap body 6 is provided outside of the air cap 5. Since the structure of such thermal spray coating gun 1 is known to those skilled in the art, further explanation thereof is omitted.

The thermal spray coating material powder is carried by inert gas such as nitrogen gas, and is supplied to the above mentioned powder projection port 2, and then is injected from the tip of the port into a combustion flame. At the same time a high pressure combustion gas supplied from the combustion gas passage 8 burns at the outer periphery of the tip of the nozzle insert 3 and the shell 4. This combustion flame is encircled by compressed air and is ejected under a high temperature and a high pressure from the air cap 5 to form a cylindrical and ultra high speed flame. The thermal spray coating material powder ejected from the tip of the port 2 is heated, melted and accelerated by the ultra high speed flame at the center of the flame, so that the melted powder is blown out with a high speed from the thermal spray coating gun 1. The droplets of the thermal spray coating material powder collide with base material 100 which is placed at a prescribed distance, e.g. 170-350mm from the gun 1. Thereby a thermal coating 102 is formed on the surface of the base material.

The thermal spray coating material powder used in the invention will now be described.

In this invention, for the thermal spray coating material powder, a mixed powder of Cu based lead bronze alloy powder and Al powder or Al based alloy powder is used. The Cu based lead bronze alloy powder contains lead which provides scuff resistance but has little mating material-attack property, that is, the characteristic to attack or cause erosion/corrosion on an object it contacts, and yet has self-lubricating properties. The Al powder or Al based alloy powder is added to the Cu based lead bronze alloy powder in the volume of 2-30 % and functions to restrain the oxidation of the lead at the time of thermal spray coating and to strengthen the bonding of the coating. Detailed explanation will be made with respect to this feature later.

The preferred Cu based lead bronze alloy powder comprises Cu based lead bronze alloy containing as its components Cu = 77-89 wt%, Sn = 4-11 wt%, Pb = 4-11 wt% and the balance being impurities of less than 1 wt%. The impurities, ordinarily Ni, Zn, Fe, Sb, Si, etc. may be exemplified. When Cu in the Cu based lead bronze alloy is less than 77 wt%, the alloy becomes brittle and on the other hand if it exceeds 89 wt%, the scuff resistance effect of other additive metals, Sn, Pb is impaired. Therefore, the amount of Cu is preferably 77-89 wt%, or more preferably 77-86 wt%. Sn dissolves in Cu in the form of a solid solution and improves hardness and tensile strength. When Sn exceeds 11 wt%,  $\delta$  phase which is brittle, is apt to be produced, and on the other hand when it is less than 4 wt%, toughness decreases. Thus, the amount of Sn is preferably 4-11 wt%, more preferably 6-9 wt%. Also, Pb is a metal having a self-lubricating property and a distinguished scuff resistance relative to a metal matrix such as martensite and carbide in carbon steel. Pb dissolves but only slightly in Cu-Sn alloy in the form of a solid solution and exists among primary crystal particles. When Pb is present in more than 11 wt%, the bonding strength of the thermal coating deteriorates, and on the other hand, when it is below 4 wt%, the self-lubricating property is not sufficient. Thus, the amount of Pb is preferably 4-11 wt%, more preferably 6-9 wt%.

The Al powder used in the invention means aluminum in which the amount of impurities is below 1.5 wt%, that is, having a purity of 98.5% or higher. Also, the Al based alloy powder used in the invention means aluminum based alloy preferably containing as its components Al = 65-95 wt%, Si = 4-30 wt%, Cu = 0.5-6 wt%, Mg = 0.3-12 wt% and the balance being impurities of less than 0.5 wt%. As the impurities, ordinarily, Fe, Zn, Mn, etc. may be exemplified.

According to the results of research and experiments by the present inventors, it was found that when a thermal spray coating is performed using Cu based lead bronze alloy, namely Cu-Sn-Pb type lead bronze, Pb within the alloy reacts with oxygen in air to form lead oxides, that is PbO, PbO<sub>2</sub>, during the thermal spray coating or forming of the coated layer, resulting in weakening of the bonding strength of the coating. Further research and experiments revealed that when Al powder which is more easily susceptible to oxidation or Al based alloy powder containing Si is mixed with and added to the Cu based lead bronze alloy powder and then is used for the thermal spray coating, the oxidation of Al and Si first takes place, resulting in the restraining of the oxidation of Pb, thus reducing the amount of lead oxides such as PbO, PbO<sub>2</sub> produced, and the bonding of the coating can be strengthened. This invention is based on such findings by the present inventors.

As further explanations on the above mentioned Al based alloy which is added to the Cu based lead bronze alloy powder, when Al is below 65 wt%, brittleness takes place, and when it exceeds 95 wt%, tensile strength is lowered, therefore, the amount of Al is preferably 65-96 wt%, more preferably 65-91 wt%. Si dissolves in Al in the form of a solid solution to improve hardness and tensile strength. However, when Si exceeds 30 wt%, a brittle phase is likely to be produced thus it should be set at 30 wt% or less. On the other hand, when it is less than 4 wt%, little improvement of hardness and tensile strength can be expected; thus Si is preferably 4-30 wt%, more preferably at 8-25 wt%. Also, Cu dissolves in Al in the form of a solid solution and enhances hardness and tensile strength. However, Cu combines itself with Al to form intermetallic compounds of  $\theta$  phase (CuAl<sub>2</sub>), so that when Cu exceeds 6 wt%, this  $\theta$  phase increases and the mechanical properties deteriorate so that the material becomes brittle, thus, Cu should be set at 6 wt% or less. On the other hand, if Cu is less than 0.5 wt%, little improvement in the hardness and tensile strength can be expected; thus Cu is preferably 0.5-6 wt%, more preferably 2-4 wt%. Further, Mg dissolves in Al in the form of a solid solution and improves hardness and tensile strength. However, Mg combines itself with Al to form intermetallic compounds of  $\beta$  phase (Al<sub>3</sub>Mg<sub>2</sub>), and if Mg exceeds 12 wt%, this  $\beta$  phase increases, resulting in a deterioration of the mechanical properties and the material becomes brittle. Therefore, Mg should be set at 12 wt% or less. On the other hand, when Mg is less than 0.3 wt%, not much improvement in the hardness and tensile strength can be expected, thus Mg is preferably 0.3-12 wt%, more preferably at 0.5-6 wt%.

As explained above, the Cu based lead bronze alloy is exposed to an oxidizing atmosphere at high temperature during the thermal spray coating and consequently lead in its components is oxidized, or further, when the Cu based lead bronze alloy collides with the base material to be thermal spray coated and the lead is exuded and overheated, lead oxides are produced. As the lead oxides are formed on the surface of the lead, the bonding among flat particles which are thermal spray coated to build up layers, is weakened. For this, when 2% by volume or more of Al or preferably Al based alloy with the above mentioned composition is added to the Cu based lead bronze alloy, the formation of such lead oxides is restrained. Therefore, by the addition of Al or Al based alloy, the peel-off of Pb from the coating can be prevented at the time of machining the coating, thus permitting sound machining and finishing without formation of voids or porosity.

As described above, when Al powder or Al based alloy powder is added to Cu based lead bronze alloy powder, the bonding strength of the coated layer increases depending on the amount added, but if the amount of Al powder or Al based alloy powder exceeds 30% by volume, a ratio of the amount of lead precipitated in the Cu based lead bronze alloy decreases and scuff resistance is lowered. Therefore, in the case where the material is used under a sliding condition with a high load, a coating with high pressure resistance is needed, and to that end, the amount of Al powder or Al alloy powder added is preferably set at 2-30% by volume, more preferably 3-11% in volume.

Particle diameters of the above mentioned Cu based lead bronze alloy, Al and Al based alloy in powder form used

in this invention are preferably 10-75  $\mu\text{m}$ , more preferably 10-60  $\mu\text{m}$ . That is, when the particle diameter exceeds 75  $\mu\text{m}$ , particle temperature during the thermal spray coating becomes low, and the amount of unmelted particles increases, therefore, the formation of a dense and fine coating becomes difficult. On the other hand, when particle diameters are smaller than 10  $\mu\text{m}$ , particles melt excessively and the content of oxides in the coating increases and the coating becomes brittle. Also, the supply of the thermal spray coating material powder deteriorates and a continuous thermal spray coating becomes difficult. Therefore, the particle diameters are set as mentioned above to 10-75  $\mu\text{m}$ , preferably 10-60  $\mu\text{m}$ , or particularly 10-45  $\mu\text{m}$  for A1 powder and A1 based alloy powder.

For the combustion gas used in the thermal spray coating method in this invention, any one of mixed gases comprising oxygen/propane, oxygen/propylene, oxygen/natural gas, oxygen/ethylene, oxygen/kerosene and oxygen/hydrogen is utilized suitably, and a flame speed of 1000-2500 m/second is obtained. When the flame speed increases, the speed of thermal spray coating particles also increases, and the bite of particles onto the base material at the time of colliding with the base material improves. In other words, the anchoring effect is enhanced, and thus overall adhesion improves. Also, when the speed of particles is high, thermal energy converted from kinetic energy at the time of collision increases, melting the uppermost surface of the base material, thus the adhesion is enhanced. The flame speed necessary for securing such adhesion is 1000 m/second or faster. On the other hand, the maximum speed of flame is limited to 2500 m/second due to the structure of the present thermal spray coating gun 1 having the above mentioned configuration. Also, the flame temperature in the combustion of mixed gas mentioned above is 2200-3000  $^{\circ}\text{C}$ .

For example, when a mixed gas of oxygen/propane is used as the combustion gas, the gas condition during the thermal spray coating is as follows: oxygen gas is set with a pressure of 9-13 Bar and a flow rate of 150-400 LPM (liter/minute), propane gas is set with a pressure of 5-8 Bar and a flow rate of 50-120 LPM, and compressed air is set with a pressure of 5-7 Bar and a flow rate of 250-700 LPM. Also, the ratio of flow rates between propane and oxygen gas is set such that propane : oxygen is 1 : 3.8-4.8 (as converted to the standard state), which provides the optimum combustion efficiency. When the ratio of oxygen relative to propane is below 3.8, the amount of unreacted propane increases, resulting in an increase in cost. Also when the ratio of oxygen relative to propane exceeds 4.8, there will be too much unreacted oxygen, resulting in oxides being produced in the coating that deteriorate the coating.

When a mixed gas of oxygen/propylene is used as the combustion gas, the gas condition during the thermal spray coating may be as follows: oxygen gas is set with a pressure of 9-13 Bar and a flow rate of 150-400 LPM, propylene gas is set with a pressure of 5-8 Bar and a flow rate of 40-130 LPM, and compressed air is set with a pressure of 5-7 Bar and a flow rate of 250-700 LPM. Also, the ratio of flow rates between propylene gas and oxygen gas is set such that propylene : oxygen is 1 : 3.5-4.5 (as converted to the standard state), which provides the optimum combustion efficiency. When the ratio of oxygen relative to propylene is below 3.5, the amount of unreacted propylene increases, resulting in an increase in cost. Also when the ratio of oxygen relative to propylene exceeds 4.5, the amount of unreacted oxygen increases, resulting in oxides being produced in the thermal coating and causing deterioration in properties of the coating.

When a mixed gas of oxygen/hydrogen is used as the combustion gas, the gas condition during the thermal spray coating may be as follows: oxygen gas is set with a pressure of 9-13 Bar and a flow rate of 150-400 LPM; hydrogen gas is set with a pressure of 8-12 Bar and a flow rate of 500-900 LPM, and compressed air is set with a pressure of 5-7 Bar and a flow rate of 250-700 LPM. Also, the ratio of flow rates between oxygen gas and hydrogen gas is set such that oxygen : hydrogen is 1 : 2.0-2.6 (as converted to the standard state), which provides the optimum combustion efficiency. When the ratio of hydrogen relative to oxygen is below 2.0, the amount of unreacted oxygen increases, resulting in oxides being produced in the coating that cause deterioration in properties of the coating. Also when the ratio of hydrogen to oxygen exceeds 2.6, the amount of unreacted hydrogen increases, resulting in an increase in cost.

In the present invention, the spraying distance at the time of thermal spray coating (distance between the thermal spray coating gun 1 and the base material to be thermal spray coated) is preferably set at 170-350 mm. The reason is that in the case where the distance is below 170 mm, the powder is not fully accelerated and heated. On the other hand, in the case where the distance exceeds 350 mm, the temperature and the speed of the powder which is once accelerated and heated are lowered, resulting in a reduction of the adhesion strength between the base material and the powder particles and of that among particles, which are not desirable.

In addition, concerning the surface of the base material 100 to be thermal spray coated, it is necessary to remove scale from a part or the whole surface of the base material to perform preliminary cleaning and surface roughening, before forming the coating in order to enlarge the adhesion surface and maintain the adhesion strength with the coating 102 at high level.

This surface roughening can be suitably conducted by a grit blast treatment, which is carried out by blasting grit of SiC, alumina, etc. to the surface of the base material to be thermal spray coated with a pressure of about 0.5 MPa. The surface of the base material after the surface roughening preferably has an uneven surface formed having a surface roughness of  $\mu\text{Rz}$  - 10-60, and more preferably of 15-40. This unevenness increases the contact area of the coating and the base material, strengthening the anchoring effect, that is, mechanical bonding. If the surface roughness is below 10  $\mu\text{Rz}$ , the anchoring effect is insufficient and thus the adhesion is lowered. On the other hand, if the surface

roughness exceeds 60 $\mu$  Rz, the surface roughness of the coating also becomes rough so as to require increased finishing work at a later stage, which is not efficient

It is desirable that a thermal spray coating is carried out after performing such blast treatment and after heating the base material to 50-150 °C. Heating to 50 °C or higher is necessary for preventing a dew condensation and increasing the adhesion. Also suppressing the heating of the base material to 150°C or below is necessary to prevent thermal deformation and strength deterioration of the base material. Further, it is necessary to control the temperature of the coating and the base material during the thermal spray coating operation to 200 °C or below, preferably to 150°C or below in order to prevent the oxidation of the coating.

Also, the thickness of the coating is preferably 0.02 mm or thicker for the securing abrasion resistance effect, and 0.5 mm or thinner for prevention of peel-off during the thermal spray coating and peel-off due to thermal stress during sliding. Also, the surface roughness after the thermal spray coating is preferably finished to Ra = 0.4-6.0 S. Ra exceeding 6.0 S leads to the impairing of scuff resistance, whereas Ra lowering 0.4 S leads to a cost increase.

Examples of the present invention will be explained in further detail.

#### Example 1

As the powder material for thermal spray coating, a mixed powder was prepared and used, which comprised 90% by volume of Cu based lead bronze alloy powder having the composition as shown in Table 1 below and 10% by volume of Al based alloy powder having the composition as shown in Table 1.

As the base material to be thermal spray coated, a swash plate having an outer diameter of 100 mm x inner diameter of 50 mm x thickness of 6 mm, for an air compressor pump was used. The material of the swash plate was SS41 (structural steel, Japanese Industrial Standards).

First, a grit blast treatment was performed as a preliminary treatment, by blowing alumina grit (particle size #20) against the surface of the swash plate with a pressure of 0.5 MPa. The surface roughness of the swash plate became  $\mu$  Rd = 45-50 with this preliminary treatment.

Next, a preliminary heating was done using the thermal spray coating gun 1 shown in Fig. 1. At this time, the thermal spray coating gun 1 was operated in such a manner that only the flame was injected under the fusion coating condition mentioned below, but without the thermal spray coating material powder supplied. The thermal spray coating distance was maintained at 300 mm. Thereby the swash plate was heated to 100°C to remove moisture, water and steam off the surface thereof.

Then, a coating was formed on the swash plate by using the thermal spray coating gun 1 under the following thermal spray coating condition.

(Thermal spray coating condition)

Combustion gas

Oxygen	pressure = 11 Bar, flow rate = 300 SLM;
Propane gas	pressure = 7 Bar, flow rate = 65 SLM; and
Air	pressure = 6 Bar, flow rate = 400 SLM

Here, "SLM" means the flow rate (liter/minute (LPM)) of gas as converted to the standard condition.

Flame temperature 2600°C  
 Flame speed 1400 m/second  
 Thermal spray coating distance 200 mm  
 Amount of thermal spray coating material powder supplied 75 g/minute

Table 1

Cu based lead bronze alloy (Particle diameter: 10-60 $\mu$ m)					
Component	Cu	Sn	Pb	Zn	Others (Fe, Sb, Si)
wt%	80.1	10.2	8.4	0.6	0.7

Table 1 (continued)

Al based lead bronze alloy (Particle diameter 10-45 $\mu$ m)					
Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)
wt%	84.3	11.3	3.6	0.5	0.3

The thickness of thus obtained thermal spray coating on the surface of the swash plate was 0.23 mm, and the surface of the coating was finished by buffing after machining so as to have a thickness of coating of 0.15 mm and a surface roughness of  $R_a = 0.6-0.8$  S. No void or porosity having 0.01 mm diameter or larger was found on the finished surface. Also, the results of SEM observation and EPMA surface analysis revealed that the amount of lead which reacted with oxygen to become lead oxides such as  $PbO$  etc., was small.

The swash plate having the thermal coating prepared as mentioned above was used to carry out a single item frictional abrasion test by pushing a shoe made of SUJ2 against the surface of the swash plate with a surface pressure or bearing pressure of 10 MPa and at the same time rotating the swash plate with a peripheral speed of 1 m/second. Also, as a comparative example, a conventional swash plate which was Sn-plated (plating thickness of 0.01 mm) on its surface was used to perform a single item frictional abrasion test under the same conditions. As a result, the conventional example with Sn-plating was worn with the maximum depth of wear of 0.01 mm or deeper and exposed the substrate SS41. In comparison, abrasion loss on the surface of the swash plate made by the present invention was 6  $\mu$ m, thus it was revealed that the latter had better abrasion resistance, scuff resistance and pressure resistance.

Examples 2-5, Comparative Examples 1-5.

As the thermal spray coating material powder, a mixed powder was prepared and used, which contains Cu based lead bronze alloy (A) having the composition as shown in Table 2(a), (b) below and Al based alloy having the composition as shown in Table 2 or A1 (B) in the mixing ratio as shown in the Table.

As the base material to be thermal spray coated, ring shaped test pieces for the frictional abrasion test which were made of S15C (Japanese Industrial Standards) and had dimensions of an outer diameter of 120 mm x inner diameter of 60 mm x thickness of 5.5 mm, and disc shaped test pieces for the pressure resistance test which were made of SS41 (Japanese Industrial Standards) and had dimensions of diameter of 30 mm x height of 25 mm, were used.

First as a preliminary treatment, a grit blast treatment was performed by blasting alumina grit (particlesize #30) onto the surfaces of these test pieces with a pressure of 0.4 MPa. The surface roughness of the test pieces became  $\mu R_z = 25-35$  with the preliminary treatment.

Next, a preheating treatment was conducted using the thermal spray coating gun 1 shown in Fig. 1. At this time, the spray coating gun 1 was operated in such a manner that only the flame was injected under the thermal spray coating condition shown below, but the thermal spray coating material powder was not supplied. The thermal spray coating distance was maintained at 300 mm. Thereby the test pieces were heated to 100°C to remove moisture, water and steam off the surfaces thereof.

Then, a coating was formed on each test piece using the thermal spray coating gun 1 under the thermal spray coating condition mentioned below.

(Thermal spray coating condition)

Combustion gas

Oxygen	Pressure = 12 Bar, flow rate = 330 SLM;
Propylene gas	Pressure = 6.5 Bar, flow rate = 75 SLM;
	and
Air	Pressure = 7 Bar, flow rate = 390 SLM

Here, "SLM" means gas the flow rate (liter/minute (LPM)) converted to the standard state.

Flame temperature 2700°C

Flame speed 1450 m/second

Thermal spray coating distance 200 mm

Amount of thermal spray coating material powder supplied 85 g/minute

Table 2-a

	Mixing ratio (Volume %)	A : Cu based lead bronze alloy B : Al or Al based alloy							
		A	Component	Cu	Sn	Pb	Zn	Others (Fe, Si, Sb)	
Example 2	A : B = 70 : 30	A	Weight %	78.6	9.5	10.8	0.7	0.4	
			Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)	
		B	Weight %	85.0	11.5	2.5	0.7	0.3	
Example 3	A : B = 90 : 10	A	Component	Cu	Sn	Pb	Zn	Others (Fe, Si, Sb)	
			Weight %	88.6	5.9	4.4	0.4	0.7	
		B	Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)	
Example 4	A : B = 95 : 5	A	Weight %	66.7	28.2	2.2	1.5	0.4	
			Component	Cu	Sn	Pb	Zn	Others (Fe, Si, Sb)	
		B	Weight %	78.3	9.8	10.9	0.5	0.5	
Example 5	A : B = 97 : 3	A	Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)	
			Weight %	78.6	14.4	5.5	1.2	0.3	
		B	Component	Cu	Sn	Pb	Zn	Others (Fe, Si, Sb)	
		A	Weight %	78.3	10.9	9.8	0.5	0.5	
			Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)	
		B	Weight %	98.8	0.25	0.4	0.05	0.5	



Table 2-b

	Mixing ratio (Volume %)	A : Cu based lead bronze alloy B : Al or Al based alloy						
		A	Component	Cu	Sn	Pb	Zn	Others (Fe, Si, Sb)
Comparative Example 1	A : B = 50 : 50	A	Weight %	78.3	10.9	9.8	0.5	0.5
			Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)
Comparative Example 2	A : B = 80 : 20	A	Weight %	98.8	0.25	0.4	0.05	0.5
			Component	Cu	Sn	Pb	Zn	Others (Fe, Si, Sb)
Comparative Example 3	A : B = 60 : 40	A	Weight %	92.1	3.3	3.1	0.5	1.0
			Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)
Comparative Example 4	A : B = 40 : 60	A	Weight %	84.6	7.1	7.0	0.4	0.9
			Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)
Comparative Example 5	A = 0 B = 100	B	Weight %	89.8	3.6	3.3	2.6	0.7
			Component	Al	Si	Cu	Mg	Others (Fe, Zn, Mn)

Thickness of the thermal spray coating of each test piece thus obtained was 0.15 mm in the ring shape test piece for the frictional abrasion test, and 0.5 mm in the disc shape test piece for the pressure resistance test. The surface of said coating of each test piece was then buffed after machining and finished to produce a coating thickness of 0.10 mm (test piece for frictional abrasion test) and 0.45 mm (test piece for pressure resistance test), and at the same time a surface roughness of  $R_a = 0.6-0.8 \text{ S}$

The disc shape test pieces for the pressure resistance test each having coating made as mentioned above were used and then compressed by a universal testing machine for measuring the pressure resistance at which the coating was sheared to peel off the base material. The results of the measuring are shown in Fig. 2.

Similarly, the ring shape test pieces for the frictional abrasion test each having coating made as mentioned above were used to measure an abrasion loss of the coating (ring) by pressing the surface of the test piece with a surface pressure of 220 MPa, by a block made of SUJ2 (Japanese Industrial Standards), and at the same time rotating the test piece with a peripheral speed of 20 m/second. The results are shown in Fig. 3

Further, a shoe made of SUJ2 was pressed with a surface pressure of 220 MPa, and by simultaneously rotating

the test piece with a peripheral speed of 20 m/second, and a load until a seizure took place which was then measured. The results are shown in Fig. 4. Also, amounts of produced PbO, PbO<sub>2</sub> on the sectional tissue of each test piece was measured by surface analysis with EPMA, revealing that the area where lead oxides were formed was smaller than that in the coating having only the Cu based lead bronze alloy powder without addition of the Al powder or Al based alloy powder.

In synthetically appraising the pressure resistance, abrasion resistance and scuff resistance from the results shown in Fig. 2-Fig. 4, it was revealed that the test pieces having the coatings shown in Examples 2, 3, 4, 5 made according to the invention were superior to those in

#### Comparative Examples 1-5

As has been explained above, since the high speed thermal spray coating method according to the present invention is constructed such that a mixed powder is used as thermal spray coating material powder, said mixed powder containing

- (A) 98-70% in volume of Cu based lead bronze alloy powder, and
- (B) 2-30% in volume of Al powder or Al based alloy powder, it can achieve a number of effects such as

- (1) Coated layers which have satisfactory abrasion resistance, scuff resistance and pressure resistance, under high speed rotation, high load and non-lubricant conditions can be thermal spray coated on the surface of the base material to be thermal spray coated at a high speed and at the same time in an easy manner;
- (2) Formation of lead oxide in the thermal spray coating is restrained, therefore a satisfactory coating can be formed, which is free from peel-off at the time of machining and capable of being soundly machine-finished without voids, and has good adhesion; and
- (3) Especially, a coating with excellent lubricity and abrasion resistance can be formed on a portion of the surface or the entire surface of a swash plate for an air compressor pump made of Al alloy, cast iron or steel based alloy.

#### Claims

1. A high speed thermal spray coating method in which a high speed flame is produced by using a combustion gas and thermal spray coating material powder is sprayed by using said high speed flame onto the surface of a base material to be thermal spray coated to form a coating on the surface of the base material, the method being characterized in that for said thermal spray coating material powder a mixed powder is used, said mixed powder containing:

- (A) 98-70% by volume of Cu based lead bronze alloy powder, and
- (B) 2-30% by volume of Al powder or Al based alloy powder.

2. A high speed thermal spray coating method according to claim 1, wherein said Cu based lead bronze alloy powder comprises Cu based lead bronze alloy containing as its components Cu = 77-89% by weight, Sn = 4-11% by weight and the balance being impurities of 1% or less by weight, said Al powder comprises Al containing less than 1.5% by weight of impurities, and said Al based alloy powder comprises Al based alloy containing as its components Al = 65-95% by weight, Si = 4-30% by weight, Cu = 0.5-6% by weight, and Mg = 0.3-12% by weight.
3. A high speed thermal spray coating method according to claim 1 or claim 2, wherein each of said Cu based lead bronze alloy powder, said Al powder and said Al based alloy powder has a particle diameter of 10-75  $\mu$ m.
4. A high speed thermal spray coating method according to claim 1, 2 or 3, wherein said base material is subjected to a grit blast treatment on the surface of the said base material so as to have a surface roughness of  $\mu$  Rz = 10-60, and is heated to 50-150°C, and then is thermal spray coated to form a coating having a thickness of 0.2-0.5 mm on the surface of said base material.
5. A high speed thermal spray coating method according to any one of claims 1 to 4, wherein said thermal spray coating is performed by using as said combustion gas any one of mixed gases comprising oxygen/propane, oxygen/propylene, oxygen/natural gas, oxygen/ethylene, oxygen/kerosene and oxygen/hydrogen to generate a high speed flame having a flame speed of 1000-2500 m/second and a flame temperature of 2200-3000°C, while main-

taining a thermal spray coating distance at 170-350 mm and controlling a coating temperature during thermal spray coating to 200°C or below

6. A high speed thermal spray coating method according to any one of claims 1 to 5 wherein said coating on the surface of the base material is finished to have a surface roughness of  $R_a = 0.4-6.0 \mu m$
7. A high speed thermal spray coating method according to any one of claims 1 to 6, wherein said base material is a swash plate for an air compressor pump made of Al alloy, cast iron or steel based alloy
8. A spray coating powder for use in a high speed thermal spray coating method, which is a mixed powder containing (A) 98-70% by volume of Cu based lead bronze alloy powder, and (B) 2-30% by volume of Al powder or Al based alloy powder.
9. A spray coating powder according to claim 8, wherein said Cu based lead bronze alloy powder comprises Cu based lead bronze alloy containing as its components Cu = 77-89% by weight, Sn = 4-11% by weight and the balance being impurities of 1% or less by weight, said Al powder comprises Al containing less than 1.5% by weight of impurities, and said Al based alloy powder comprises Al based alloy containing as its components Al = 65-95% by weight, Si = 4-30% by weight, Cu = 0.5-6% by weight, and Mg = 0.3-12% by weight, and preferably each of said Cu based lead bronze alloy powder, said Al powder and said Al based alloy powder has a particle diameter of 10-75  $\mu m$ .
10. A spray coated article such as a swash plate, made by the method of any of claims 1 to 7.

FIG. 1

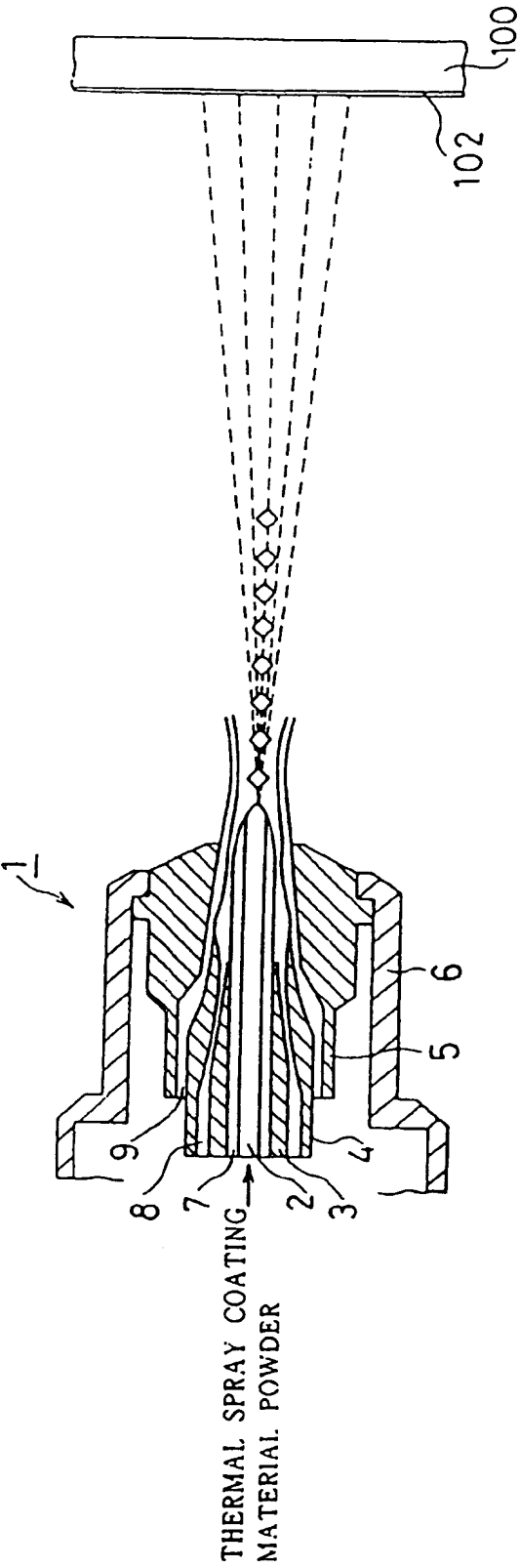


FIG. 2

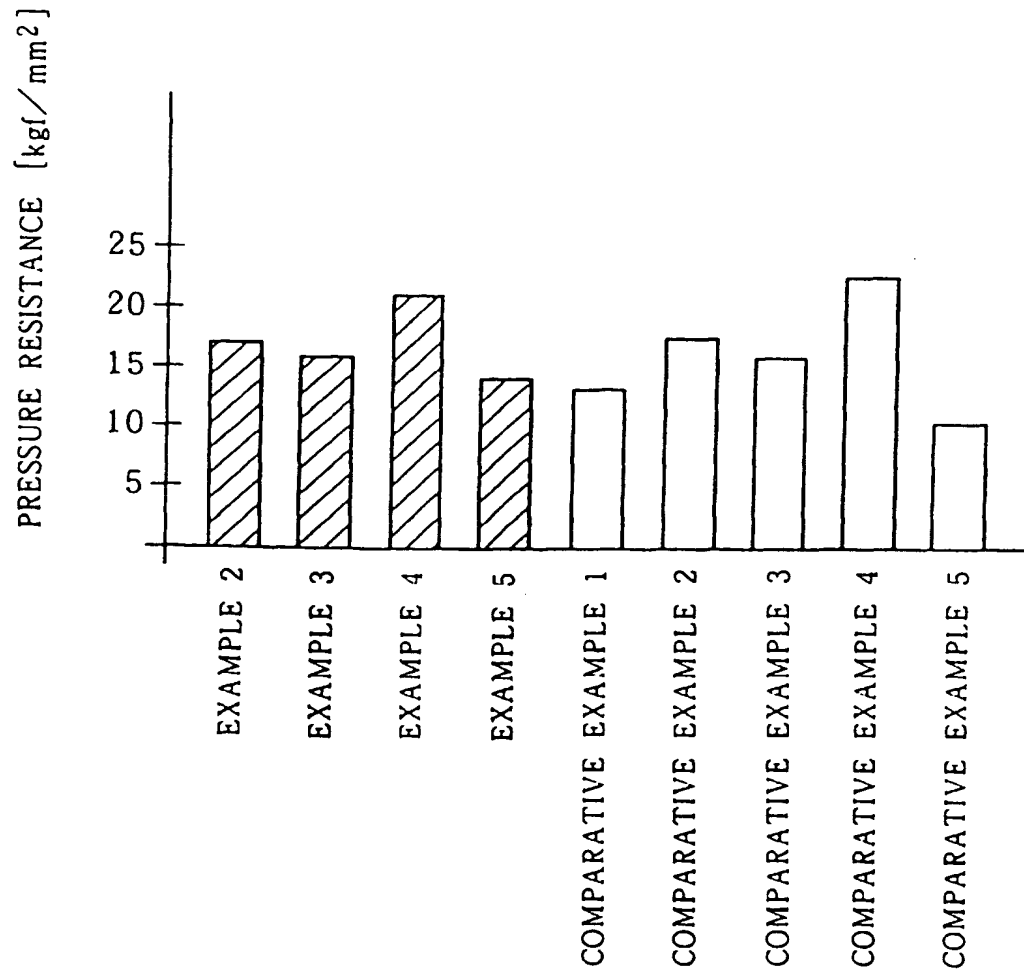


FIG. 3

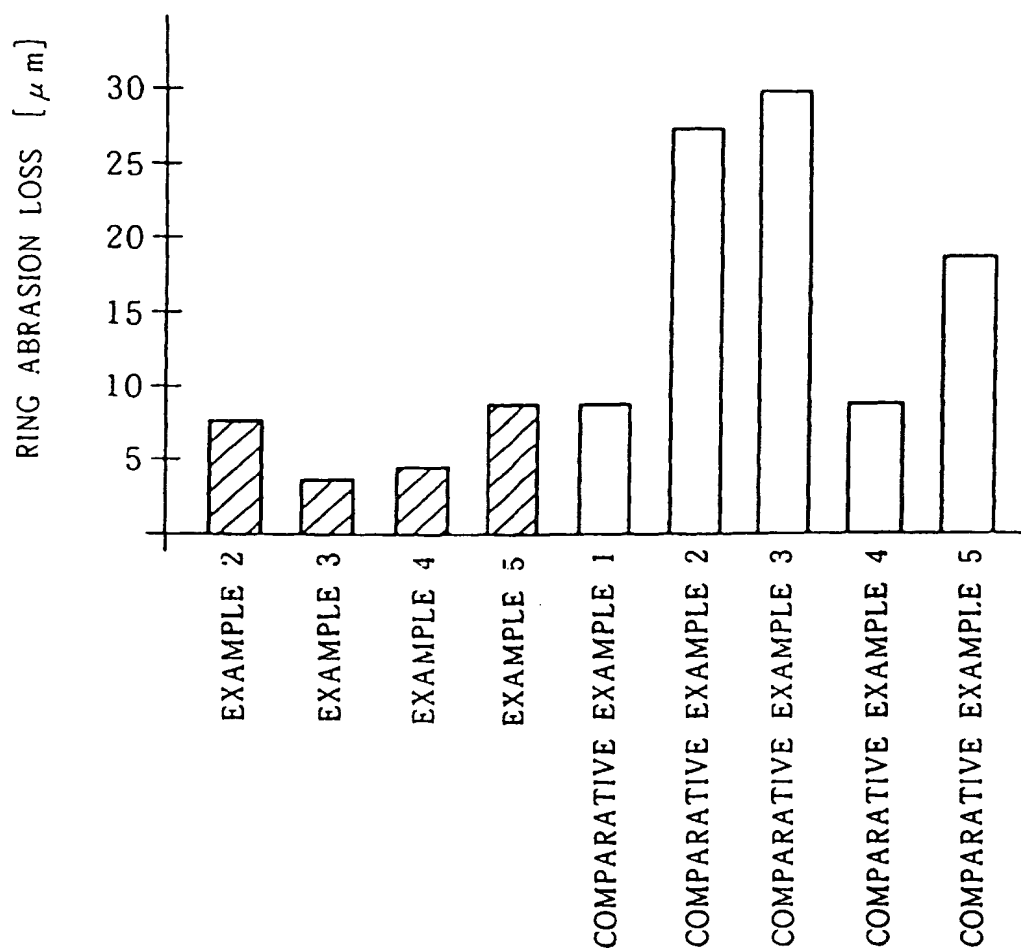
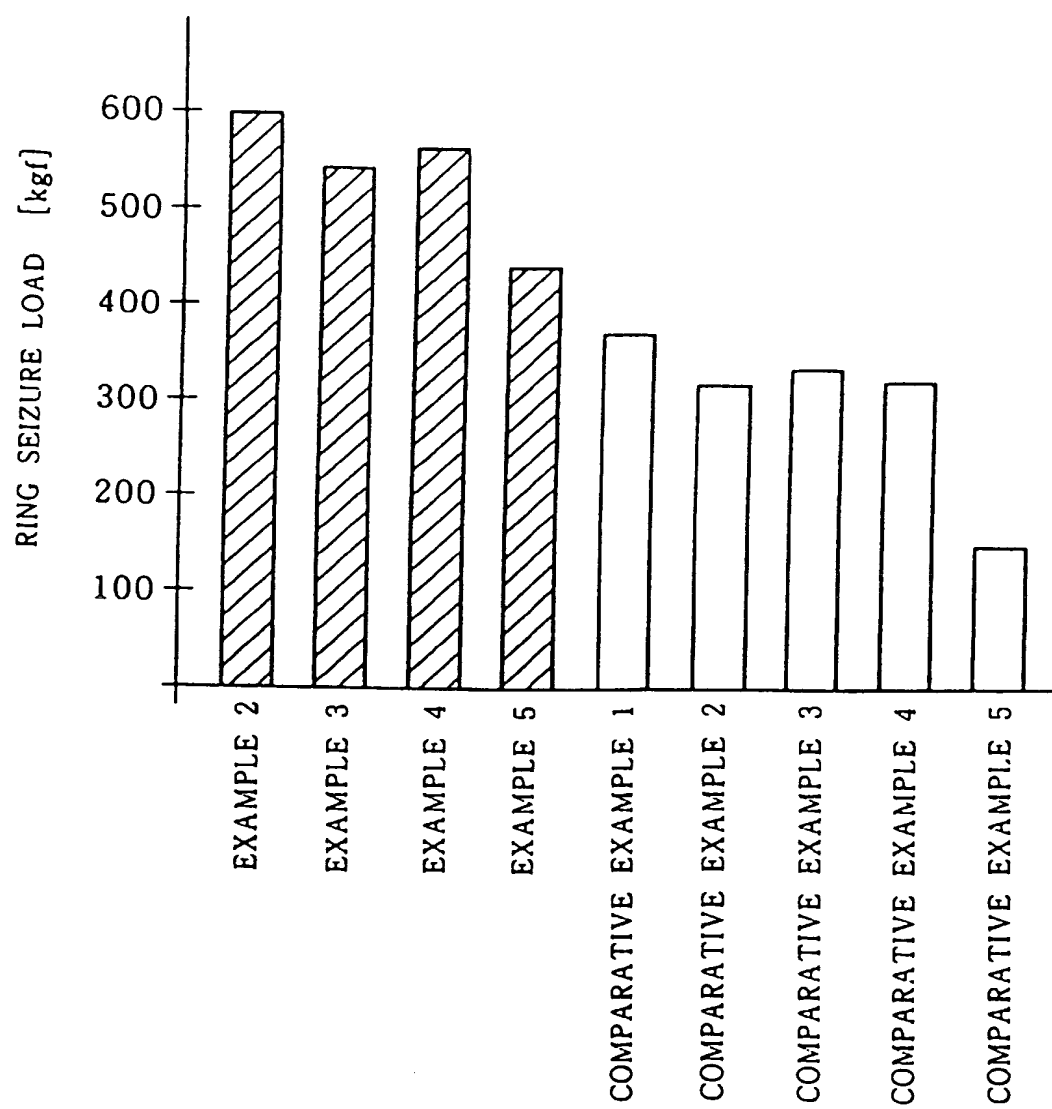


FIG. 4



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(71) Applicant: Sulzer Metco Japan Ltd.  
Tokyo 102 (JP)

(72) Inventors:  
• Masahiro, Nakagawa  
Chiyoda-ku, Tokyo 102 (JP)

- Sasaki, Matisumasa  
Chiyoda-ku, Tokyo 102 (JP)
- Mima, Hidetada  
Chiyoda-ku, Tokyo 102 (JP)
- Hashimoto, Hiroyuki  
Chiyoda-ku, Tokyo 102 (JP)
- Hotta, Toshio  
Chiyoda-ku, Tokyo 102 (JP)
- Miyazaki, Tomoko  
Chiyoda-ku, Tokyo 102 (JP)

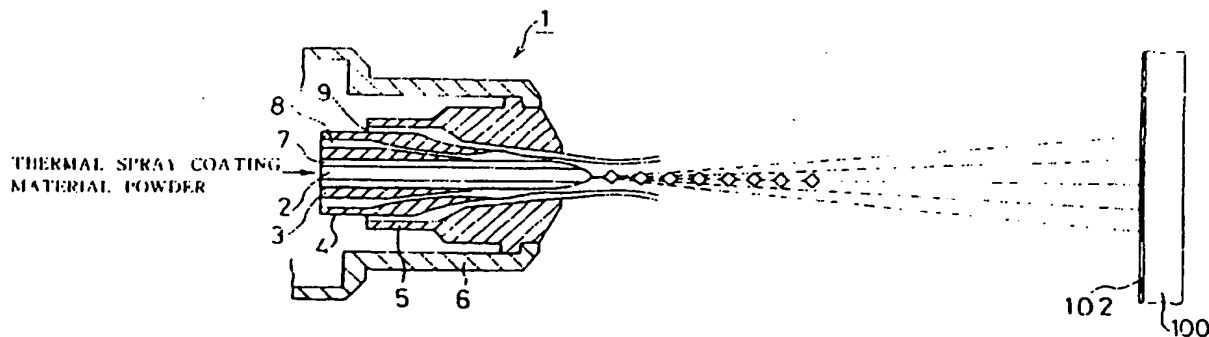
(74) Representative: Harvey, David Gareth et al  
Graham Watt & Co.  
Riverhead  
Sevenoaks Kent TN13 2BN (GB)

### (54) High speed thermal spray coating method

(57) In a thermal spray coating method, a high speed flame is produced by using a combustion gas and then thermal spray coating material powder is sprayed by flame gun (1) onto a receiving surface (100) of a base material by using the high speed flame to form a coating

(102) on the base material. As the thermal spray coating material powder, a mixed powder is used, which contains (A) 98-70% by volume of Cu based lead bronze alloy powder and (B) 2-30% by volume of A1 powder or A1 based alloy powder.

FIG. 1



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## EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A	US 5 385 789 A (RANGASWAMY SUBRAMANIAM ET AL) * claim 1 *	1	C23C4/08 C23C4/12
A	DATABASE WPI Section Ch. Week 7806 Derwent Publications Ltd., London, GB: Class M13, AN 78-11201A XF002057883 - & JP 52 155 139 A (HITACHI HUNMATSU) . 23 December 1977 * abstract *	1	
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			TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
			C23C F04B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 5 March 1998	Examiner Gregg, N
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